

**USE INFORMATION AND APPLICATION MONITORING  
RECOMMENDATIONS FOR THE PESTICIDE ACTIVE  
INGREDIENT METHOMYL AND THE AMBIENT AIR  
MONITORING RECOMMENDATIONS FOR METHOMYL AND  
CARBARYL**

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**ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM**

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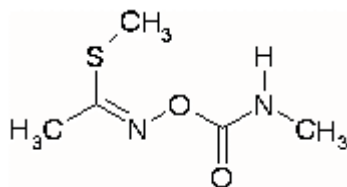
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## A. BACKGROUND

This recommendation contains general information regarding the physical-chemical properties of methomyl and its reported historical uses as a pesticide in California. The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

### Physical-Chemical Properties

Figure 1. Chemical structure of methomyl.



Methomyl (Chemical name: S-methyl-N((methylcarbamoyl)oxy)thioacetimidate; Molecular structure:  $C_5H_{10}N_2O_2S$ ) (Figure 1) is a white crystalline solid with a slightly sulfurous odor with a solubility of 5.8 g/100 g water (DuPont 2005). It is stable under normal temperatures when dry, but thermal decomposition and combustion will produce hazardous gases. These may include sulfur oxides, methyl isocyanate and hydrogen cyanide. Table 1 lists physical-chemical properties of methomyl.

Table 1. Physical and chemical properties of methomyl (Hazardous Substances Data Bank. 2007; Crop Protection Handbook, 2007).

Chemical name	methomyl
Trade names <sup>†</sup>	Lannate
CAS Registry number	16752-77-5
Molecular formula	$C_5H_{10}N_2O_2S$
Molecular Weight	162.2 g/mol
Melting Point	78 – 79 °C
Vapor Pressure	$5.4 \times 10^{-6}$ mmHg (25 °C)
Specific Gravity	1.2946 (24 °C)
Water Solubility	58,000 mg/L (25 °C)
Henry's Law Constant	$1.90 \times 10^{-10}$ atm-m <sup>3</sup> /mol (25 °C)
Soil Adsorption Coefficient ( $K_{oc}$ )	43.3 cm <sup>3</sup> /g
Field Dissipation Half-life	54 days, sandy loam soil
Octanol / Water Partition Coefficient ( $K_{ow}$ )	0.60
Hydrolysis half life	30 days

<sup>†</sup> Disclaimer: The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

## **B. CHEMICAL USES IN CALIFORNIA**

E.I. Du Pont De Nemours & Co. (Du Pont) currently registers two products containing methomyl — Lannate SP (soluble powder) and Lannate LV (liquid concentrate). Lannate SP contains a higher percentage of methomyl than Lannate LV (90% versus 29%) and accounts for the majority of agricultural use in California. These products are applied directly to soil either by aerial application or using ground spray and are used as pesticides to control a wide range of insects including thrips, bugs, aphids, beetles, moths, diptera and ant-hymenoptera on a variety of commodities. (DPR Product/Label Database <http://www.cdpr.ca.gov/docs/label>). They are restricted use pesticides.

Methomyl is an N-methyl carbamate insecticide with anticholinesterase activity and as such carries a Poison/Danger signal word on the label. It is fatal if swallowed and may be fatal if inhaled. According to the label Lannate SP, the more widely used of the formulations, is a dry powder to be dissolved in water for application by mechanical ground or air equipment only. Hand-held equipment is prohibited for applications to crops and the pesticide must not be applied through any type of irrigation system. It should not be applied by ground equipment within 25 feet, or by air within 100 feet of lakes, reservoirs, rivers, estuaries, commercial fish ponds and natural, permanent streams, marshes or natural, permanent ponds.

Total annual use for methomyl was 264,226lbs in 2004 and 349,447lbs in 2005 (Table 2), a 32% increase. Use in the top 14 counties, based upon pounds a.i. applied for each year, are represented in Table 2. These counties account for almost 90% of the total use overall. Monthly use in the top three counties, Fresno, Monterey and Imperial, are shown in Table 3. These three counties had the highest usage in both 2004 and 2005, and in both years applications of methomyl accounted for 57% and 59% of the total amount applied statewide, respectively. The greatest amount of pounds a.i. applied in Fresno and Monterey counties occurred in the months June through October, with more than twice the amount applied in June and July of 2005 than in the same months in 2004. In 2004, methomyl use in Imperial County was relatively consistent throughout the year with the lowest amounts applied in August and September. In 2005, however, application rates peaked in June, November and December.

In 2004 and 2005 methomyl was used on 88 and 89 commodities (or sites). The twelve commodities receiving the most methomyl were alfalfa, cantaloupe, celery, corn for human consumption, grapes, lettuce – both head and leaf, onion, strawberry, sugar beet and tomatoes – fresh and canning, which accounted for 79% of the total pounds of methomyl applied (Table 4).

Table 2. Annual Methomyl Use by the Top 14 Counties Overall (Pounds Active Ingredient)

<b>County</b>	<b>2004</b>	<b>2005</b>	<b>Total</b>
COLUSA	4,630	4,460	9,090
CONTRA COSTA	8,197	9,278	17,474
FRESNO	60,009	93,925	153,934
IMPERIAL	36,900	50,547	87,447
KERN	15,314	12,931	28,245
KINGS	5,983	10,145	16,128
MADERA	0	9,151	9,151
MERCED	13,389	31,201	44,590
MONTEREY	54,590	63,455	118,045
SAN BENITO	4,778	0	4,778
SAN JOAQUIN	7,473	8,306	15,778
SANTA BARBARA	7,640	7,682	15,322
TULARE	6,698	13,437	20,136
VENTURA	6,236	0	6,236
Total for Top 14 Counties	231,838	314,517	546,355
% of CA Total	88	90	89
Total Statewide Use	264,226	349,447	613,672

Table 3. Monthly Agricultural Methomyl Use by the Top 3 Counties (2004 - 2005), (Pounds Active Ingredient)

<b>COUNTY/YEAR</b>	<b>JAN</b>	<b>FEB</b>	<b>MAR</b>	<b>APR</b>	<b>MAY</b>	<b>JUN</b>	<b>JUL</b>	<b>AUG</b>	<b>SEPT</b>	<b>OCT</b>	<b>NOV</b>	<b>DEC</b>	<b>TOTAL</b>
Fresno 2004	0	0	3,175	1,153	3,759	9,212	13,051	12,088	8,162	8,140	1,256	13	60,009
Fresno 2005	0	35	2,681	543	7,902	21,870	26,298	12,862	7,677	13,325	733	0	93,925
<b>Total</b>	<b>0</b>	<b>35</b>	<b>5,856</b>	<b>1,696</b>	<b>11,661</b>	<b>31,083</b>	<b>39,349</b>	<b>24,950</b>	<b>15,839</b>	<b>21,464</b>	<b>1,989</b>	<b>13</b>	<b>153,934</b>
Monterey 2004	74	117	1,063	3,512	5,579	8,373	13,496	10,122	8,358	3,328	551	18	54,590
Monterey 2005	7	209	2,181	2,114	3,662	9,576	10,916	16,126	12,924	5,228	458	53	63,455
<b>Total</b>	<b>81</b>	<b>326</b>	<b>3,244</b>	<b>5,626</b>	<b>9,242</b>	<b>17,950</b>	<b>24,412</b>	<b>26,248</b>	<b>21,281</b>	<b>8,555</b>	<b>1,009</b>	<b>71</b>	<b>118,045</b>
Imperial 2004	2,958	2,131	2,273	2,703	4,635	4,114	4,979	1,255	1,012	4,842	3,728	2,270	36,900
Imperial 2005	3,592	2,353	3,020	3,293	4,790	9,260	4,212	3,661	759	2,498	6,688	6,420	50,547
<b>Total</b>	<b>6,550</b>	<b>4,485</b>	<b>5,292</b>	<b>5,996</b>	<b>9,425</b>	<b>13,374</b>	<b>9,191</b>	<b>4,916</b>	<b>1,771</b>	<b>7,340</b>	<b>10,416</b>	<b>8,691</b>	<b>87,447</b>

Table 4. Annual Cropland Use of Methomyl by Top 12 Commodities, (Pounds Active Ingredient)

<b>Crop</b>	<b>2004</b>	<b>2005</b>	<b>Total</b>
ALFALFA	21,121	60,287	81,408
CANTALOUPE	6,453	5,927	12,380
CELERY, GENERAL	6,499	6,729	13,227
CORN, HUMAN CONSUMPTION	32,057	39,942	71,999
GRAPES	15,422	12,884	28,306
LETTUCE, HEAD	29,115	39,255	68,371
LETTUCE, LEAF	23,159	29,892	53,051
ONION	10,833	19,832	30,664
STRAWBERRY	21,399	16,534	37,933
SUGARBEET, GENERAL	20,138	23,457	43,595
TOMATO	5,389	8,037	13,426
TOMATOES, FOR PROCESSING/CANNING	13,689	19,398	33,087
Total for Top 12 Commodities	205,275	282,173	487,447
% of CA Total	78	81	79
Total Statewide Use	264,226	349,447	613,672

### C. APPLICATION SITE AIR MONITORING RECOMMENDATIONS

Growers in Fresno County used the most methomyl in both 2004 and 2005. The majority of applications occurred during June, July and August to treat over 40 different crop types. Corn, tomatoes, alfalfa, onion, cantaloupe and sugarbeet accounted for 75% of methomyl use over 2004-05.

According to the product label for Lannate SP, the highest application rate of no more than 6.3 lbs a.i./acre can be applied to tomatoes, followed by cantaloupe (5.4 lbs a.i./acre), sugarbeet (4.5 lbs a.i./acre) onions and alfalfa (3.6 lbs a.i./acre), therefore DPR recommends that monitoring occur in a one of the crops with the highest application rate during the summer of 2007. Application sites for these commodities ranged from 3 to 238 acres treated with an average of 94 acres (DPR PUR Database). However, entries in the PUR database may reflect multiple applications to the same site, resulting in high reported acreage. DPR therefore recommends that the selected monitoring site be 94 to 238 acres. If a site this size cannot be located, a smaller site is acceptable but should be at least 10 acres. Figures 2 and 3 show use amounts and locations in Fresno County during June - August of 2004 and 2005.

A minimum of eight samplers should be positioned around the application site, one on each side of the site and one at each corner. A ninth replicate sampler should be co-located at one position.

Ideally, samplers should be placed a minimum of 20 meters from the application area. DPR recommends coordination with the county agricultural commissioner to select the most appropriate sampling sites. If a site is located on a private property, permission from the property owner must be obtained. Air samples should be taken before, during, and after application and for three Daytime/Overnight sampling periods as in the following schedule.

<b>Sample period begins:</b>	<b>Sample duration time</b>
Background (pre-application)	Minimum 12 – 24 hours
Application	Start of application until 1 hour after end of application
End of application (post-application)	End of application until 1 hour before sunset
1 hour before sunset	Overnight <sup>1</sup> until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise
1 hour after sunrise	Daytime until 1 hour before sunset
1 hour before sunset	Overnight until 1 hour after sunrise

<sup>1</sup>All overnight samples must include the period from one hour before sunset to one hour after sunrise.

Field spikes and trip blanks should be prepared in the laboratory and run in the field with the samples for quality assurance.

DPR requests the following information be included in the monitoring report:

- 1) an accurate record of the application site, including topographic features
- 2) an accurate record of the positions of the monitoring equipment with respect to the application site, including the exact direction and distance of the samplers from the edge of the application site
- 3) an accurate record of pesticide application, including application dosage or quantity of pesticide applied, application starting and ending time, method and application rate, etc.
- 4) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles with respect to North (identified as either true or magnetic North)
- 5) if applicable, meteorological data collected at 1-minute intervals including wind speed and direction, humidity, air temperature, and comments regarding degree of cloud cover.

Figure 2.

## Fresno County - Methomyl Use June, July & August 2004

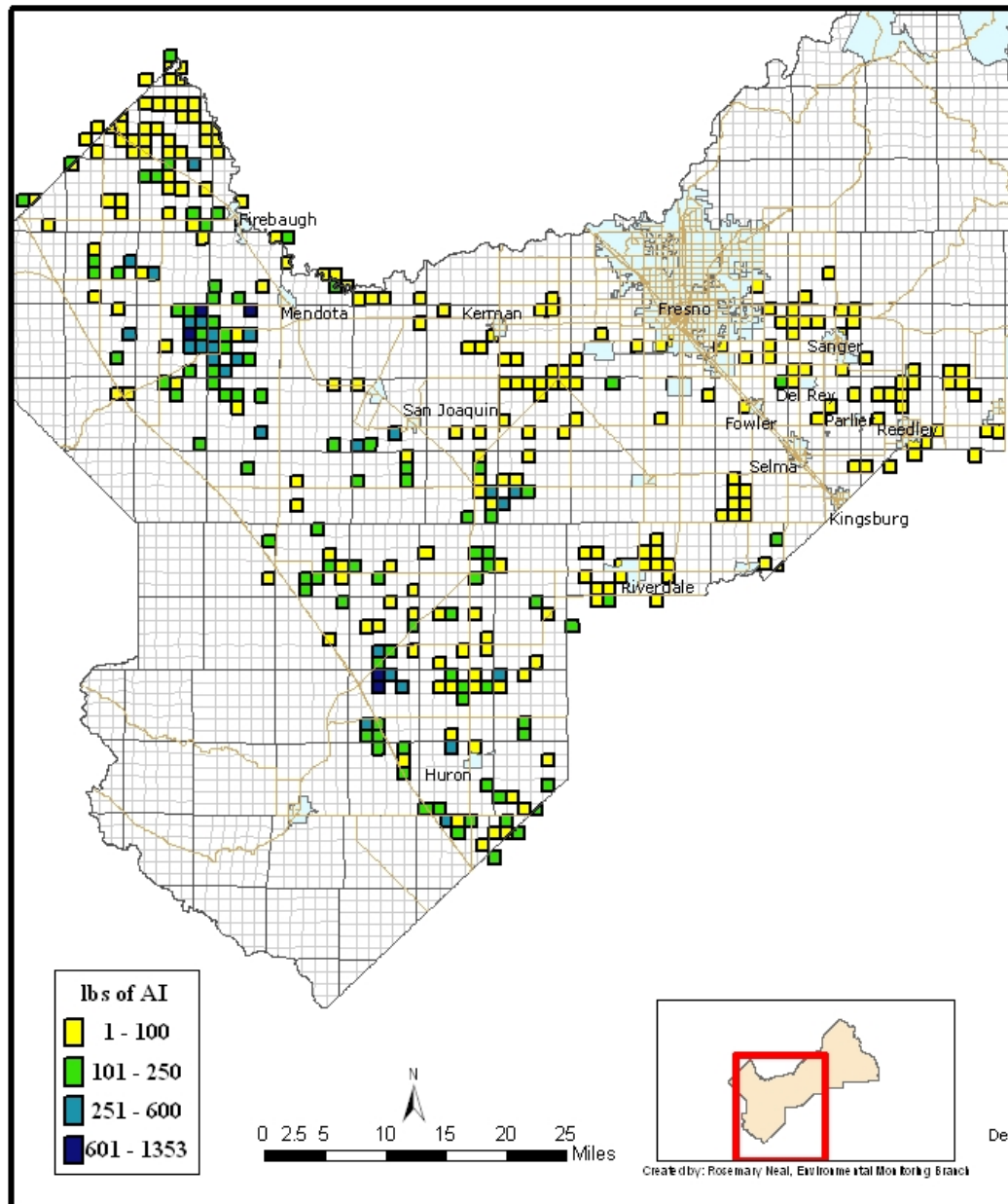
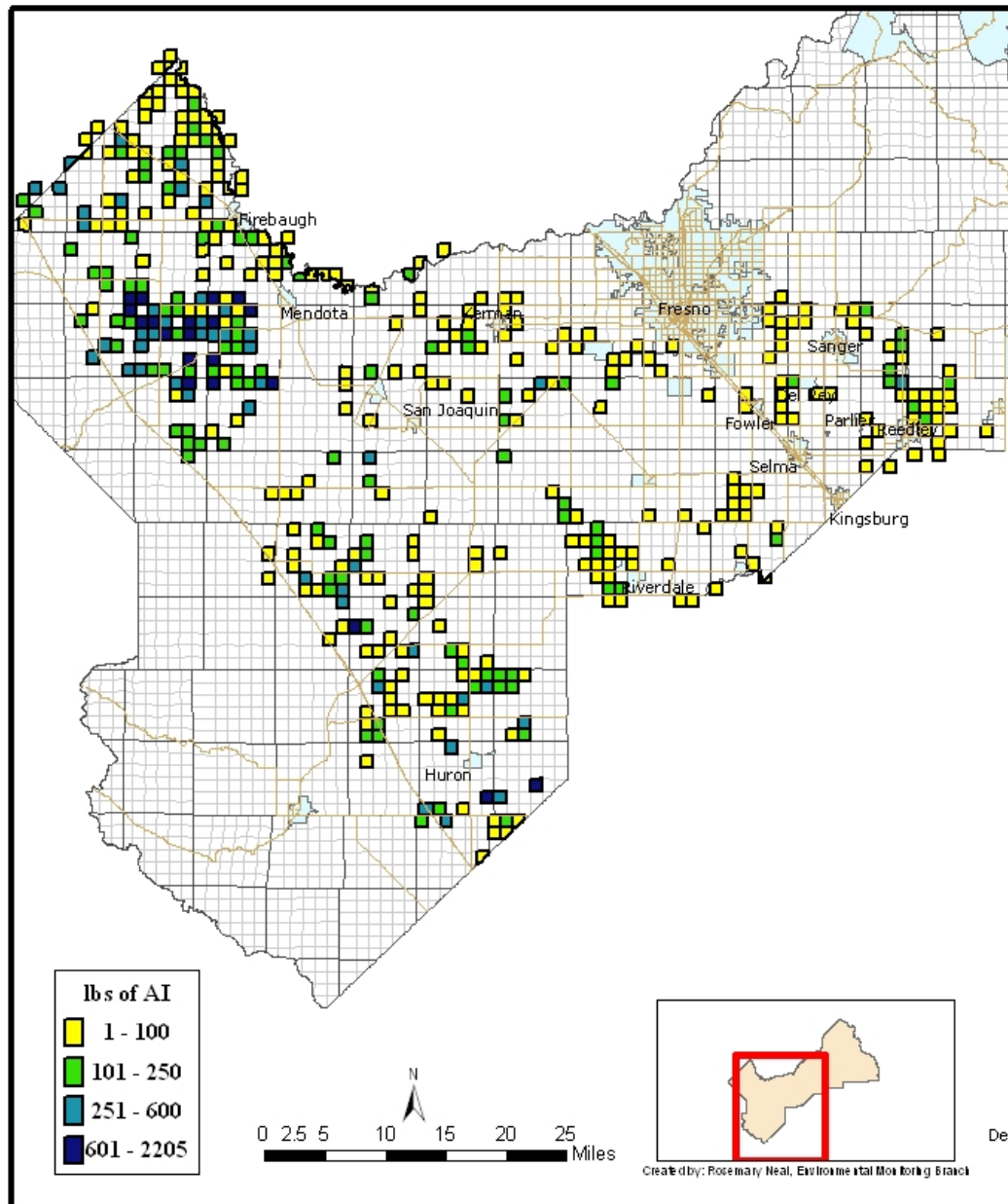




Figure 3.

## Fresno County - Methomyl Use June, July & August 2005



## **D. AMBIENT AIR MONITORING RECOMMENDATIONS**

As part of the Cal/EPA Environmental Justice Action Plan, DPR recommends ambient air monitoring of methomyl in rural communities to address the environmental risk factors that impact children's health.

Because they are located closer to agricultural fields, California rural communities may have higher concentrations of methomyl in ambient air compared to urban communities. The selection of communities is based on objective data, using criteria that can be quantified, validated, and verified, providing a more transparent and fair selection process. DPR selected 139 communities in thirteen counties for evaluation based on their proximity to methomyl applications - Fresno, Imperial, Kern, Kings, Madera, Merced, Monterey, San Benito, San Luis Obispo, Santa Barbara, Santa Cruz, Stanislaus and Tulare . The communities are identified by name in the 2000 U.S. Census, and are also included in a spatial dataset distributed by the U.S. Census Bureau for use in a Geographic Information System (GIS).

Each of the 139 communities were rated on the following categories and subcategories:

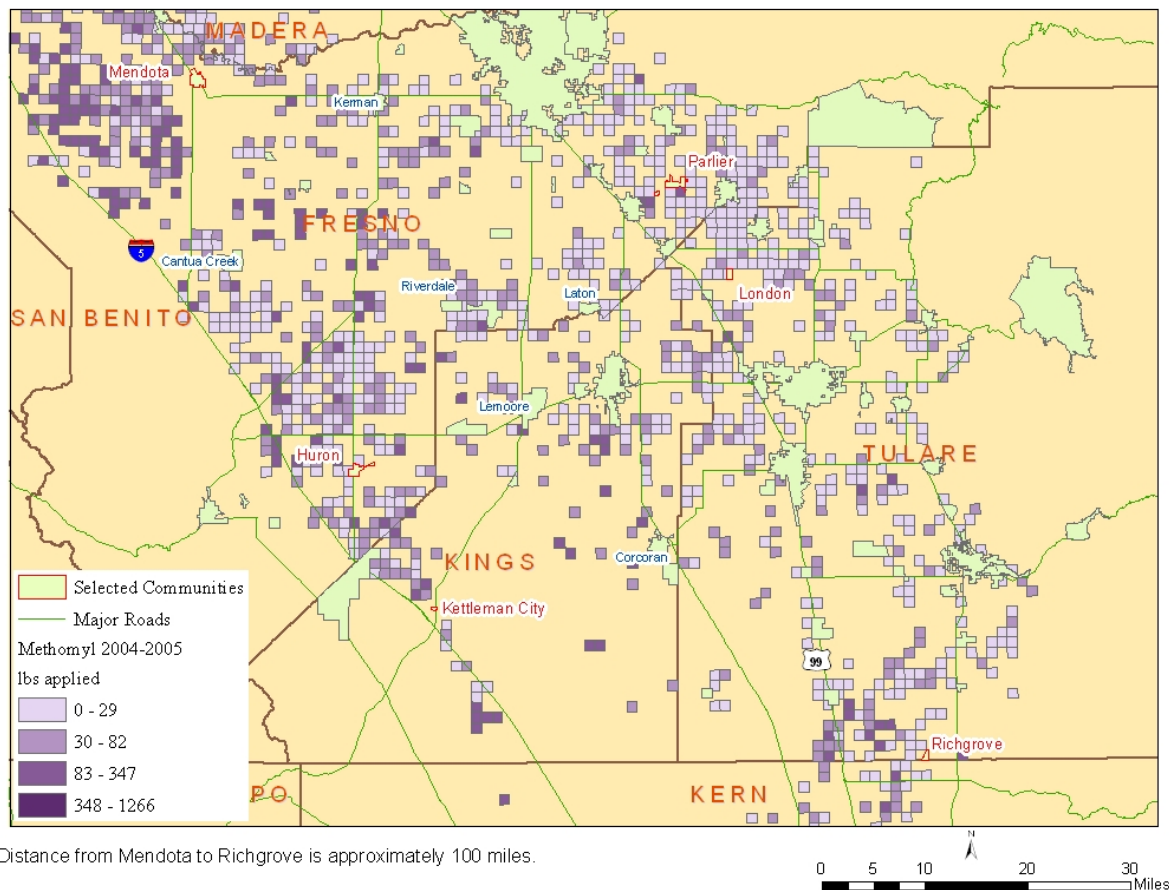
- Environmental justice factors
  - Population density of children (less than 18 years old)
  - Median family income
  - Hispanic population percentage
  - Non-white population percentage
- Pesticide use
  - Regional (within 5 miles of community) use density of methomyl
  - Local (within 1 mile of community) use density of methomyl

In most cases, the subcategory ratings are based on density per square mile rather than numerical totals. This minimizes the effect of the size of the community in the ratings. Without this adjustment, large communities such as Fresno would show much greater child population and pesticide use in comparison to communities with small areas. The area of each community is determined by the U.S. Census Bureau and is delineated in the spatial dataset that was used in this study. A GIS was used to calculate the amount of methomyl applied within 1 mile and 5 miles of the edge, or boundary, of each community using a buffering algorithm. Communities were ranked according to the density of methomyl applications (lbs/square mile of community area) for both the 1-mile (local) and 5-mile (regional) zones for 2004 and 2005. The two major category ratings (environmental justice and pesticide use) were then added together for an overall community rating. This system gives equal weight to each of the both major categories.

Six sampling sites (five air monitoring sites and one urban background site) should be selected in relatively high-population areas or in areas frequented by people (e.g., schools or school district offices, fire stations, or other public buildings). The ambient air monitoring sites should be located in areas where there is high use of methomyl and where environmental justice factors are highest. Methomyl use in 2004-2005 and community environmental justice factors indicate that ambient air monitoring should occur over an 8-week period during June, July and August in the San Joaquin Valley region. The communities of Huron, Mendota and Parlier in Fresno County,

and Richgrove in Tulare County, and Kettleman City in Kings County, plus an urban background site are suggested as potential monitoring locations (Figure 3). The background samples should be collected in an area distant to applications the target pesticide, such as the San Joaquin Valley APCD located in Fresno, CA. At each sampling site, four 24-hour samples should be collected per week during the sampling period. DPR recommends close coordination with local school districts or state/local fire jurisdictions to select the best sampling sites.

Figure 4. Suggested Locations for Ambient Air Monitoring of Methomyl.



Since both methomyl and carbaryl can be sampled and analyzed in the same sample at minimal extra cost, DPR requests that carbaryl concentrations also be determined. Like methomyl carbaryl is also a wide-spectrum carbamate insecticide that controls over 100 species of insects on a wide variety of agricultural commodities. Total annual use for carbaryl was 240,109lbs in 2004 and 190,600lbs in 2005 (Table 5), showing a 20% decrease in applications over the two year period. Use in the top 14 counties, based upon pounds a.i. applied for each year, are represented in Table 5. These counties account for over 80% of the total use of carbaryl overall. The top four counties include Fresno and Tulare in which five of the six suggested communities for methomyl ambient air monitoring are located. Monthly use for 2004-2005 in the Kern, Tulare, San Joaquin and Fresno are shown in Table 6. The greatest amount of pounds of active ingredient applied in Tulare County occurred in the months July and August and monthly usage

more than doubled in 2005 compared to 2004. In Fresno County carbaryl use peaked in April and May and also in August and September, with more than 25% more used in 2005 than in 2004 overall.

Table 5. Annual Carbaryl Use by the Top 14 Counties Overall (Pounds Active Ingredient)

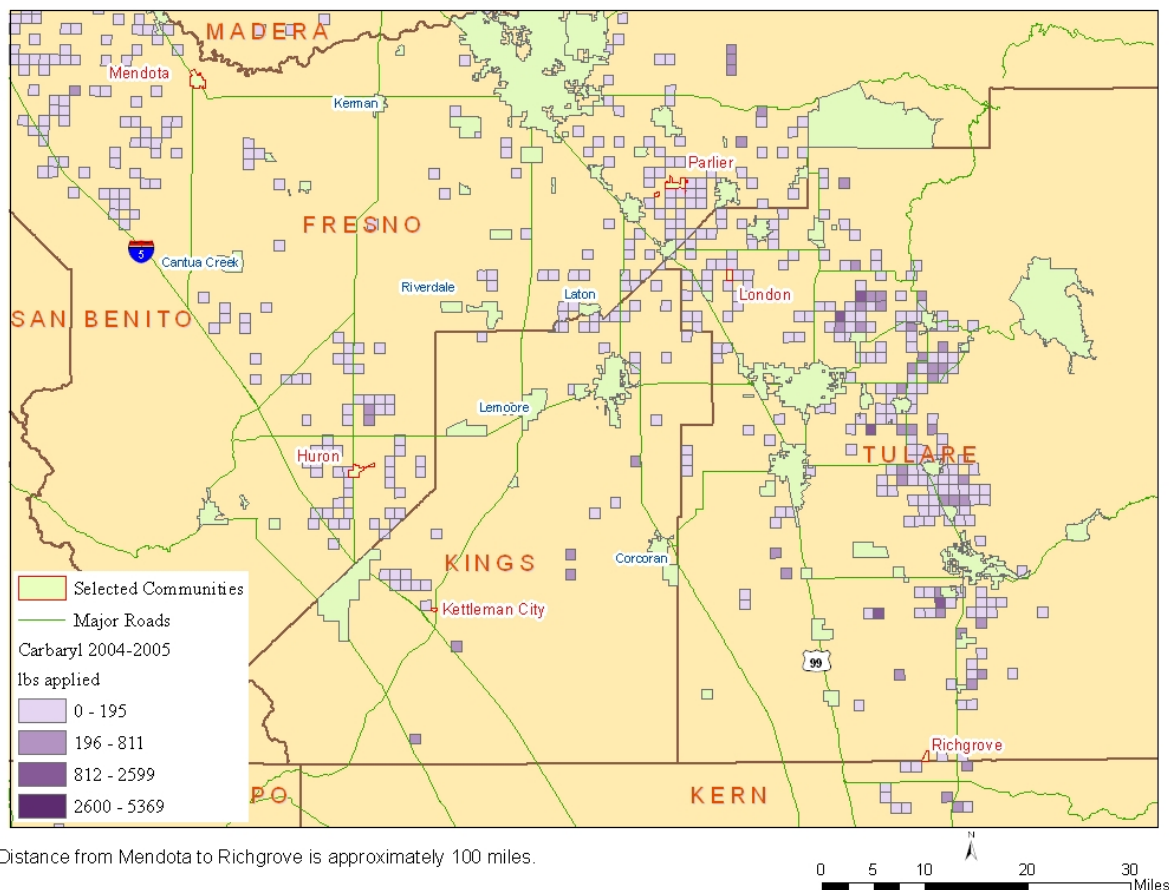
<b>County</b>	<b>2004</b>	<b>2005</b>	<b>Total</b>
FRESNO	12367	15813	28180
INYO	20708	47	20755
KERN	42051	33397	75448
MADERA	7379	11109	18488
MERCED	4405	5970	10375
MONTEREY	5649	2452	8101
SACRAMENTO	4343	6928	11271
SAN BENITO	6631	2956	9587
SAN BERNARDINO	4504	9076	13579
SAN JOAQUIN	25570	11674	37244
STANISLAUS	28688	3280	31967
SUTTER	7761	5668	13430
TULARE	25694	42156	67850
VENTURA	3967	3813	7779
Total for Top 14 Counties	199715	154339	354054
% of CA Total	83	81	82
Total Statewide Use	240109	190600	430709

Table 6. Monthly Agricultural Carbaryl Use by the Top 4 Counties (2004 - 2005), (Pounds Active Ingredient)

<b>COUNTY/YEAR</b>	<b>JAN</b>	<b>FEB</b>	<b>MAR</b>	<b>APR</b>	<b>MAY</b>	<b>JUN</b>	<b>JUL</b>	<b>AUG</b>	<b>SEPT</b>	<b>OCT</b>	<b>NOV</b>	<b>DEC</b>	<b>TOTAL</b>
Kern 2004	37	1758	2763	3186	1778	759	11201	19631	442	16	480	42051	60009
2005		95	1695	2608	419	3137	4687	11641	7689	1056	371	33397	93925
<b>Total</b>	<b>37</b>	<b>1853</b>	<b>4458</b>	<b>5793</b>	<b>2196</b>	<b>3896</b>	<b>15888</b>	<b>31272</b>	<b>8131</b>	<b>1071</b>	<b>851</b>	<b>75448</b>	<b>153934</b>
Tulare 2004	16	191	330	560	3815	3953	5189	4431	3646	3010	552		25694
2005		51	134	160	1464	3705	14176	18504	2656	676	605	24	42156
<b>Total</b>	<b>16</b>	<b>242</b>	<b>464</b>	<b>720</b>	<b>5279</b>	<b>7658</b>	<b>19365</b>	<b>22935</b>	<b>6303</b>	<b>3686</b>	<b>1157</b>	<b>24</b>	<b>67850</b>
San Joaquin 2004	28	2	1920	6893	1995	10418	3648	140	295	231			25570
2005			1038	4788	2357	1569	980	522	248	44	127	1	11674
<b>Total</b>	<b>28</b>	<b>2</b>	<b>2958</b>	<b>11681</b>	<b>4352</b>	<b>11987</b>	<b>4628</b>	<b>662</b>	<b>542</b>	<b>275</b>	<b>127</b>	<b>1</b>	<b>37244</b>
Fresno 2004			1731	3131	2317	1333	1214	2123	495	0	20	4	12367
2005	3	14	675	2629	2641	2077	1680	3019	3000	75			15813
<b>Total</b>	<b>3</b>	<b>14</b>	<b>2405</b>	<b>5759</b>	<b>4959</b>	<b>3410</b>	<b>2894</b>	<b>5142</b>	<b>3495</b>	<b>75</b>	<b>20</b>	<b>4</b>	<b>28180</b>

The map in figure 5 shows the proximity of the proposed communities to carbaryl applications in 2004 and 2005.

Figure 5. Proximity of the Proposed Communities to Carbaryl Applications in 2004 and 2005.



In addition to the primary samples, replicate (co-located) samples are needed for four dates at each sampling location. Field spike samples should be collected at the same environmental conditions (e.g., temperature, humidity, exposure to sunlight) and monitoring study conditions (e.g., air flow rates, sample transportation and storage) as those occurring at the time of ambient air sampling. Target 24-hour quantitation limit of  $0.01 \mu\text{g}/\text{m}^3$  for methomyl are recommended (Warmerdam, 2007). Additionally, we request that you provide in the ambient monitoring report: 1) the proximity of the sampler to the treated or potentially treated fields, including the distance and direction, 2) the distance the sampler is located above the ground, and 3) a map of the monitoring site locations.

## **E. SAFETY RECOMMENDATIONS**

The product label for Lannate SP carries a danger/poison warning. The pesticide is fatal if swallowed, may be fatal if inhaled or absorbed through eyes, and is harmful if absorbed through the skin. Applicators and handlers must wear long-sleeved shirt and long pants, chemical resistant gloves category A (such as butyl rubber, natural rubber, neoprene rubber or nitrile rubber), all >14 mls, shoes plus socks, and protective eyewear. For exposures in enclosed areas, a respirator with an organic vapor-removing cartridge must be worn. For outdoor exposures, a dust/mist filtering respirator is required. In addition to the equipment listed above, cleaners and repairers of application equipment must wear chemical resistant footwear and a chemical resistant apron. Any protective equipment, clothing or other absorbent materials that have been drenched or heavily contaminated with this pesticide should be discarded. All other clothing and equipment should be cleaned and washed after use. Re-entry period for any person other than applicators and handlers is generally 48 hours.

## **F. REFERENCES**

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